

(19) World Intellectual Property  
Organization  
International Bureau



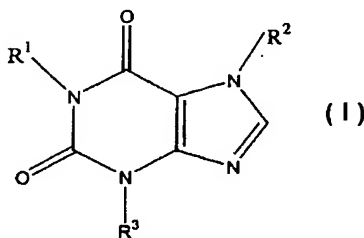
(43) International Publication Date  
15 January 2004 (15.01.2004)

PCT

(10) International Publication Number  
**WO 2004/004672 A1**

- (51) International Patent Classification<sup>7</sup>: **A61K 7/06, 7/09**
- (21) International Application Number:  
PCT/EP2003/006648
- (22) International Filing Date: 25 June 2003 (25.06.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
02254722.8 5 July 2002 (05.07.2002) EP
- (71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NI, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only): **UNILEVER N.V.** [NL/NL]; Unilever N.V., Weena 455, NL-3013 AL Rotterdam (NL).
- (71) Applicant (for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London, Greater London EC4 4BQ (GB).
- (71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).
- (72) Inventors; and  
(75) Inventors/Applicants (for US only): **KHOSDEL, Ezat** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **WARD, Sheila, Anne** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).
- (74) Agent: **TANSLEY, Sally**; Unilever Research & Development Vlaardingen, P.O. Box 137, NL-3130 AT Vlaardingen (NL).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HAIR TREATMENT COMPOSITIONS CONTAINING XANTHINE AND ALPHA HYDROXY ACID



(57) Abstract: The invention provides a hair treatment composition such as a shampoo or conditioner suitable for topical application to style hair and in particular to lengthening the hair. The composition comprises an  $\alpha$ -hydroxy acid and/or its salt and a xanthine preferably having the following formula.

- 1 -

## HAIR TREATMENT COMPOSITIONS CONTAINING XANTHINE AND ALPHA HYDROXY ACID

## FIELD OF THE INVENTION

5

The invention relates to hair treatment compositions. The compositions are particularly suitable to style and lengthen hair.

## 10 BACKGROUND AND PRIOR ART

For centuries long hair has been a desirable attribute. To achieve this straightening devices are sold that mechanically lengthen and straighten the hair, a selection  
15 of such devices are disclosed in EP 0 511 892 and WO12/32381. An alternative to the above mechanical approach to lengthen the hair is to stimulate hair growth using chemical hair growth stimulants, such products are disclosed in EP 0 897 712 and WO92/07877.

20

The use of xanthines in hair and skin pigmentation is described in US 5470579. US 4931066 discloses that xanthines can be used together with other compounds in hair dyeing.

25

Xanthines have also been claimed as being useful in the treatment of hair loss. For example, WO 85/05270, WO 84/04038, FR 2 751 541 and WO 85/05272 all disclose hair loss treatments containing caffeine or theophylline as phosphodiesterase inhibitors. A hair nourishing lotion or

- 2 -

shampoo containing caffeine and the hair loss treatment compound minoxidil is described in JP 04-193821.

The present application discloses formulations and processes for lengthening hair. The invention has the further advantages that it prevents the hair frizzing and increasing in volume. Yet another advantage is that it increases the hair's susceptibility and hold to styling in humid conditions.

#### DESCRIPTION OF THE INVENTION

In a first aspect, the present invention provides a method of treating hair comprising the step of applying to the hair a leave on hair treatment composition comprising:

- i) an  $\alpha$ -hydroxy acid and/or its salt; and
- ii) a xanthine, a substituted xanthine or mixtures thereof

A further aspect of the invention is the use of

- i) a  $\alpha$ -hydroxy acid and/or its salt; and
- ii) a xanthine, a substituted xanthine or mixtures thereof

for styling hair, in particular lengthening, reducing the volume and increasing the high humidity style retention of the hair.

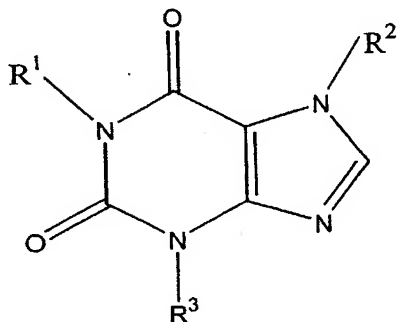
- 3 -

Detailed Description of the Invention

The present invention is based on the finding that Xanthine and alpha-hydroxy acid combinations are particularly useful in styling hair, lengthening hair, reducing its volume and increasing the high humidity style retention.

Xanthines

Preferred xanthines (the term xanthines are taken as meaning xanthines and substituted xanthines), are compounds having formula I



Formula I

in which  $R^1$ ,  $R^2$  and  $R^3$  are independently selected from H, substituted or unsubstituted  $C_1$ - $C_5$  alkyl groups, substituted or unsubstituted  $C_2$ - $C_5$  alkenyl groups, aryl groups arylalkyl groups or mixtures thereof,. It is preferable if the substituted groups discussed above are amine or hydroxy groups.

It is advantageous if  $R^1$ ,  $R^2$  and  $R^3$  are H,  $C_1$ - $C_5$  alkyl,  $C_2$ - $C_5$  alkenyl or mixtures thereof, it is particularly preferred if  $R^1$ ,  $R^2$  and  $R^3$  are independently selected from H, methyl groups or mixtures thereof.

- 4 -

Most preferred are substituted xanthines such as caffeine, dyphylline, cafaminol theophylline, aminophylline and theobromine. Of these, caffeine is particularly preferred.

5 The Xanthines may be in the form of a salt. The cosmetically acceptable salts of the xanthines of formula (I) are salts, which are non-toxic to humans in the context of the uses according to the invention. The nature of the salt will depend on the acidic or basic groups present in the xanthines  
10 which will depend, in turn, on their precise structural formula. Suitable acid addition salts include, for example, hydrochlorides, sulphates, phosphate, carboxylates (including acetates, citrates, tartarates, malates, malonates, maleates, lactates, succinates, and fumarates). Suitable base salts  
15 include, for example, ammonium salts and alkali metal salts (such as sodium and potassium salts). Suitable salts can be obtained by methods well-known to those skilled in the art.

Cosmetically acceptable solvates are similarly obtained by  
20 conventional methods. Suitable solvates include, for example, hydrates.

Xanthines can be produced synthetically or extracted from natural products, such as plant extracts. For example,  
25 certain xanthines can be obtained from cacao beans, tea leaves and cola beans. Xanthines may be used in the present invention in substantially pure form, in the form of unpurified natural extracts, or as a mixture of substantially pure form and natural extract.

- 5 -

Xanthines may be used in the present invention singly or together with one or more other different xanthines.

5 The hair treatment composition of the invention preferably comprises from 0.1 to 20 wt% of xanthine/substituted xanthine in the total formulation.

#### $\alpha$ -Hydroxy acid

10 The formulations of the invention comprise an  $\alpha$  -Hydroxy acid. The hydroxy acid and/or its salt is preferably a bis ( $\alpha$  -hydroxy acid) and/or its salt.  
The  $\alpha$  -hydroxy acid can comprise one or more carboxylic acid groups, at least one of these carboxylic acid groups should  
15 have an  $\alpha$  -hydroxy group.

It is particularly preferred an  $\alpha$  -hydroxy acid and/or its salt if optically active is in the L-form such as those derived from natural sources, particularly preferred  $\alpha$  -  
20 hydroxy acid are citric acid and tartaric acid and/or their salts.

The amount of  $\alpha$  -Hydroxy acid i) is from 0.1 to 20 wt% in the total formulation.

25

The total amount of the xanthine and  $\alpha$  -Hydroxy acid in hair treatment compositions of the invention is generally from 0.2 to 40 wt%, preferably from 1 to 10 wt%, more preferably from 2 to 5 wt%.

30

- 6 -

The weight ratio of xanthine to  $\alpha$  -Hydroxy is preferably from 1:0.001 to 0.001:1, preferably from 1:0.01 to 0.01:1, most preferably from 3:1 to 1:3.

## 5 Product Form

The final product form of hair treatment compositions according to the invention may suitably be, for example, shampoos, conditioners, sprays, mousses, gels, waxes or  
10 lotions. Particularly preferred product forms are, post-wash conditioners (leave-in) and hair treatment products such as hair essences.

Shampoo compositions preferably comprise one or more  
15 cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair. Further surfactants may be present as emulsifiers.

Suitable cleansing surfactants, are selected from anionic,  
20 amphoteric and zwitterionic surfactants, and mixtures thereof. The cleansing surfactant may be the same surfactant as the emulsifier, or may be different.

### Anionic Cleansing Surfactant

25 Shampoo compositions according to the invention will typically comprise one or more anionic cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair.

30

- 7 -

Examples of suitable anionic cleansing surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from 1 to 10 ethylene oxide or propylene oxide units per molecule.

Typical anionic cleansing surfactants for use in shampoo compositions of the invention include sodium oleyl sulphosuccinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium cocoyl isethionate, sodium lauryl isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, sodium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3), ammonium lauryl sulphate and ammonium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3).

The total amount of anionic cleansing surfactant in shampoo compositions of the invention is generally from 5 to 30, preferably from 6 to 20, more preferably from 8 to 16 wt%.



- 8 -

Co-surfactant

The shampoo composition can optionally include co-surfactants, preferably an amphoteric or zwitterionic surfactant, which can be included in an amount ranging from 0 to about 8, preferably from 1 to 4 wt%.

Examples of amphoteric and zwitterionic surfactants include, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinate, alkyl carboxyglycinates, alkyl amphopropionates, alkylamphoglycinates, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Typical amphoteric and zwitterionic surfactants for use in shampoos of the invention include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.

Another preferred co-surfactant is a nonionic surfactant, which can be included in an amount ranging from 0 to 8, preferably from 2 to 5 wt%.

For example, representative nonionic surfactants that can be included in shampoo compositions of the invention include condensation products of aliphatic ( $C_8 - C_{18}$ ) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups.

30

- 9 -

Further nonionic surfactants which can be included in shampoo compositions of the invention are the alkyl polyglycosides (APGs). Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block  
5 of one or more glycosyl groups. Preferred APGs are defined by the following formula:



10 wherein R is a branched or straight chain  $C_5$  to  $C_{20}$  alkyl or alkenyl group, G is a saccharide group and n is from 1 to 10.

Other sugar-derived nonionic surfactants which can be included in shampoo compositions of the invention include the  
15  $C_{10}$ - $C_{18}$  N-alkyl ( $C_1$ - $C_6$ ) polyhydroxy fatty acid amides, such as the  $C_{12}$ - $C_{18}$  N-methyl glucamides, as described for example in WO 92 06154 and US 5 194 639, and the N-alkoxy polyhydroxy fatty acid amides, such as  $C_{10}$ - $C_{18}$  N-(3-methoxypropyl) glucamide.

20 The shampoo composition can also optionally include one or more cationic co-surfactants included in an amount ranging from 0.01 to 10, more preferably from 0.05 to 5, most preferably from 0.05 to 2 wt%. Useful cationic surfactants are described hereinbelow in relation to conditioner  
25 compositions.

The total amount of surfactant (including any co-surfactant, and/or any emulsifier) in shampoo compositions of the invention is generally from 5 to 50, preferably from 5 to  
30 30, more preferably from 10 to 25 wt%.

- 10 -

Cationic Polymer

A cationic polymer is a preferred ingredient in shampoo  
5 compositions of the invention, for enhancing conditioning  
performance of the shampoo.

Suitable cationic nitrogen polymers are described in the CTFA  
Cosmetic Ingredient Directory, 3rd edition

The cationic conditioning polymer will generally be present  
10 in compositions of the invention at levels of from 0.01 to 5,  
preferably from 0.05 to 1, more preferably from 0.08 to 0.5  
wt%.

Conditioning Surfactant

15

Conditioner compositions usually comprise one or more  
conditioning surfactants, which are cosmetically acceptable  
and suitable for topical application to the hair.

20 Suitable conditioning surfactants are selected from cationic  
surfactants, used singly or in admixture.

Cationic surfactants useful in compositions of the invention  
contain amino or quaternary ammonium hydrophilic moieties,  
25 which are positively charged when, dissolved in the aqueous  
composition of the present invention.

The most preferred cationic surfactants for conditioner  
compositions of the present invention are monoalkyl

- 11 -

quaternary ammonium compounds in which the alkyl chain length is C16 to C22.

Examples of suitable cationic surfactants include quaternary ammonium compounds, particularly trimethyl quaternary compounds.

Preferred quaternary ammonium compounds include cetyltrimethylammonium chloride, behenyltrimethylammonium chloride (BTAC), cetylpyridinium chloride, tetramethylammonium chloride, tetraethylammonium chloride, octyltrimethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, octyldimethylbenzylammonium chloride, decyldimethylbenzylammonium chloride, stearyldimethylbenzylammonium chloride, didodecyldimethylammonium chloride, dioctadecyldimethylammonium chloride, tallowtrimethylammonium chloride, cocotrimethylammonium chloride, PEG-2 oleylammonium chloride and salts of these where the chloride is replaced by halogen, (e.g. , bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, or alkylsulphate. Further suitable cationic surfactants include those materials having the CTFA designations Quaternium-5, Quaternium-31 and Quaternium-18. Mixtures of any of the foregoing materials may also be suitable. A particularly useful cationic surfactant for use in hair conditioners of the invention is cetyltrimethylammonium chloride, available commercially, for example as GENAMIN CTAC, ex Hoechst Celanese.

- 12 -

Salts of primary, secondary, and tertiary fatty amines are also suitable cationic surfactants.

In the conditioners of the invention, the level of cationic surfactant is preferably from 0.01 to 10, more preferably 0.05 to 5, most preferably 0.1 to 2 wt% of the total composition.

#### Fatty Materials

10

Conditioner compositions of the invention preferably additionally comprise fatty materials. By "fatty material" is meant a fatty alcohol, an alkoxyated fatty alcohol, a fatty acid or a mixture thereof.

15

(Or propoxylated) fatty alcohols having from about 12 to about 18 carbon atoms in the alkyl chain can be used in place of, or in addition to, the fatty alcohols themselves. Suitable examples include ethylene glycol cetyl ether, polyoxyethylene (2) stearyl ether, polyoxyethylene (4) cetyl ether, and mixtures thereof.

20

The level of fatty alcohol material in conditioners of the invention is suitably from 0.01 to 15, preferably from 0.1 to 10, and more preferably from 0.1 to 5 wt%. The weight ratio of cationic surfactant to fatty alcohol is suitably from 10:1 to 1:10, preferably from 4:1 to 1:8, optimally from 1:1 to 1:7, for example 1:3.

30

- 13 -

Optional Ingredients**Suspending Agents**

5

In a preferred embodiment, the hair treatment composition, especially if it is a shampoo composition, further comprises from 0.1 to 5 wt% of a suspending agent.

10 **Silicone Conditioning Agents**

The compositions of the invention can contain, emulsified droplets of a silicone-conditioning agent, for enhancing conditioning performance.

15

Suitable silicones include polydiorganosiloxanes, in particular polydimethylsiloxanes which have the CTFA designation dimethicone. Also suitable for use compositions of the invention (particularly shampoos and conditioners) are polydimethyl siloxanes having hydroxyl end groups, which have the CTFA designation dimethiconol. Also suitable for use in compositions of the invention are silicone gums having a slight degree of cross-linking, as are described for example in WO 96/31188.

25

A further preferred class of silicones for inclusion in shampoos and conditioners of the invention are amino function.

- 14 -

The total amount of silicone is preferably from 0.01 to 10 %wt of the total composition more preferably from 0.3 to 5, most preferably 0.5 to 3 wt% is a suitable level.

5    (ii)    **Non-silicone Oily Conditioning Components**

Compositions according to the present invention may also comprise a dispersed, non-volatile, water-insoluble oily conditioning agent.

10

By "insoluble" is meant that the material is not soluble in water (distilled or equivalent) at a concentration of 0.1% (w/w), at 25°C.

15    Suitable oily or fatty materials are selected from hydrocarbon oils, fatty esters and mixtures thereof.

**Adjuvants**

20    The compositions of the present invention may also contain adjuvants suitable for hair care. Generally such ingredients are included individually at a level of up to 2, preferably up to 1 wt% of the total composition.

25    Suitable hair care adjuvants, include amino acids, sugars and ceramides.

**Styling Polymers**

The hair styling polymer is preferably present in the  
30    compositions of the invention in an amount of from 0.001% to

- 15 -

10% by weight, more preferably from 0.1% to 10% by weight, such as from 1% to 8% by weight.

Hair styling polymers are well known. Suitable hair styling  
5 polymers include commercially available polymers that contain moieties that render the polymers cationic, anionic, amphoteric or nonionic in nature. Suitable hair styling polymers include, for example, block and graft copolymers. The polymers may be synthetic or naturally derived.

10

Examples of anionic hair styling polymers are:

copolymers of vinyl acetate and crotonic acid;

15

terpolymers of vinyl acetate, crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid such as vinyl neodecanoate;

20

copolymers of methyl vinyl ether and maleic anhydride (molar ratio about 1:1) wherein such copolymers are 50% esterified with a saturated alcohol containing from 1 to 4 carbon atoms such as ethanol or butanol;

25

acrylic copolymers containing acrylic acid or methacrylic acid as the anionic radical-containing moiety with other monomers such as: esters of acrylic or methacrylic acid with one or more saturated alcohols having from 1 to 22 carbon atoms (such as methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, t-butyl acrylate, t-butyl methacrylate, n-butyl methacrylate,  
30 n-hexyl acrylate, n-octyl acrylate, lauryl methacrylate and



- 16 -

behenyl acrylate); glycols having from 1 to 6 carbon atoms (such as hydroxypropyl methacrylate and hydroxyethyl acrylate); styrene; vinyl caprolactam; vinyl acetate; acrylamide; alkyl acrylamides and methacrylamides having 1 to 8 carbon atoms in the alkyl group (such as methacrylamide, t-butyl acrylamide and n-octyl acrylamide); and other compatible unsaturated monomers. The additional styling polymer may also contain grafted silicone, such as polydimethylsiloxane.

10

Specific examples of suitable anionic hair styling polymers are:

RESYN® 28-2930 available from National Starch (vinyl acetate/crotonic acid/vinyl neodecanoate copolymer);

ULTRAHOLD® 8 available from BASF (CTFA designation Acrylates/acrylamide copolymer);

20 the GANTREZ®ES series available from ISP Corporation esterified copolymers of methyl vinyl ether and maleic anhydride).

Other suitable anionic hair styling polymers include carboxylated polyurethanes. Carboxylated polyurethane resins are linear, hydroxyl-terminated copolymers having pendant carboxyl groups. They may be ethoxylated and/or propoxylated at least at one terminal end. The carboxyl group can be a carboxylic acid group or an ester group, wherein the alkyl moiety of the ester group contains one to three carbon atoms. The carboxylated polyurethane resin can also be a copolymer

30

- 17 -

of polyvinylpyrrolidone and a polyurethane, having a CTFA designation PVP/polycarbamyl polyglycol ester. Suitable carboxylated polyurethane resins are disclosed in EP-A-0619111 and US Patent No. 5,000,955. Other suitable hydrophilic polyurethanes are disclosed in US Patent Nos. 3,822,238; 4,156,066; 4,156,067; 4,255,550; and 4,743,673.

Amphoteric hair styling polymers which can contain cationic groups derived from monomers such as t-butyl aminoethyl methacrylate as well as carboxyl groups derived from monomers such as acrylic acid or methacrylic acid can also be used in the present invention. One specific example of an amphoteric hair styling polymer is Amphomer® (Octylacrylamide/ acrylates/butylaminoethyl methacrylate copolymer) sold by the National Starch and Chemical Corporation.

Examples of nonionic hair styling polymers are homopolymers of N- vinylpyrrolidone and copolymers of N-vinylpyrrolidone with compatible nonionic monomers such as vinyl acetate. Nonionic polymers containing N- vinylpyrrolidone in various weight average molecular weights are available commercially from ISP Corporation - specific examples of such materials are homopolymers of N-vinylpyrrolidone having an average molecular weight of about 630,000 sold under the name PVP K-90 and are homopolymers of N-vinylpyrrolidone having an average molecular weight of about 1,000,000 sold under the name of PVP K-120.

- 18 -

Other suitable nonionic hair styling polymers are cross-linked silicone resins or gums. Specific examples include rigid silicone polymers such as those described in EP-A-0240350 and cross-linked silicone gums such as those  
5 described in WO 96/31188.

Examples of cationic hair styling polymers are copolymers of amino-functional acrylate monomers such as lower alkyl aminoalkyl acrylate, or methacrylate monomers such as  
10 dimethylaminoethyl methacrylate, with compatible monomers such as N-vinylpyrrolidone, vinyl caprolactam, alkyl methacrylates (such as methyl methacrylate and ethyl methacrylate) and alkyl acrylates (such as ethyl acrylate and n-butyl acrylate).

15 Specific examples of suitable cationic polymers are:

copolymers of N-vinylpyrrolidone and dimethylaminoethyl methacrylate, available from ISP Corporation as Copolymer  
20 845, Copolymer 937 and Copolymer 958;

copolymers of N-vinylpyrrolidone and dimethylaminopropylacrylamide or methacrylamide, available from ISP Corporation as Styleze® CC10;

25 copolymers of N-vinylpyrrolidone and dimethylaminoethyl methacrylate;

copolymers of vinylcaprolactam, N-vinylpyrrolidone and  
30 dimethylaminoethylmethacrylate;

- 19 -

Polyquaternium-4 (a copolymer of diallyldimonium chloride and hydroxyethylcellulose);

Polyquaternium-11 (formed by the reaction of diethyl  
5 sulphate and a copolymer of vinyl pyrrolidone and  
dimethyl aminoethylmethacrylate), available from ISP as  
Gafquat® 734, 755 and 755N, and from BASF as Luviquat®  
PQ11;

10 Polyquaternium-16 (formed from methylvinylimidazolium  
chloride and vinylpyrrolidone), available from BASF as  
Luviquat® FC 370, FC 550, FC 905 and HM-552;

15 Polyquaternium-46 (prepared by the reaction of  
vinylcaprolactam and vinylpyrrolidone with  
methylvinylimidazolium methosulphate), available from BASF  
as Luviquat®Hold.

Examples of suitable naturally-derived polymers include  
20 shellac, alginates, gelatins, pectins, cellulose derivatives  
and chitosan or salts and derivatives thereof. Commercially  
available examples include Kytamer® (ex Amerchol) and Amaze®  
(ex National Starch).

25 Also suitable for use as additional styling polymers in the  
compositions of the invention are the ionic copolymers  
described in WO 93/03703, the polysiloxane-grafted polymers  
disclosed in WO 93/23446, the silicone-containing  
polycarboxylic acid copolymers described in WO 95/00106 or  
30 WO 95/32703, the thermoplastic elastomeric copolymers

- 20 -

described in WO 95/01383, WO 95/06078, WO 95/06079 and WO 95/01384, the silicone grafted adhesive polymers disclosed in WO 95/04518 or WO 95/05800, the silicone macro-grafted copolymers taught in WO 96/21417, the silicone macromers of  
5 WO 96/32918, the adhesive polymers of WO 98/48770 or WO 98/48771 or WO 98/48772 or WO 98/48776, the graft polymers of WO 98/51261 and the grafted copolymers described in WO 98/51755.

10 The invention will now be further illustrated by the following, non-limiting Examples.  
Examples of the invention are illustrated by a number, Comparative Examples are illustrated by a letter.  
All percentages quoted are by weight based on total weight  
15 unless otherwise stated.

### EXAMPLES

#### Examples A, B, 1 and 2

20

Formulations according to the invention are given below:

25

30

- 21 -

Chemical Name	Example A	Example 1	Example B	Example 2
Cetearyl Alcohol -CSA	0g	0	5.00	5.00
Cetrimonium Chloride - CTAC	0	0	1.30	1.30
Glyceryl Stearate	0	0	0.60	0.60
Methyl Paraben	0	0	0.20	0.20
Mineral Oil	0	0	0.30	0.30
Glycerin	0	0	1.0	1.0
DC 1784 silicone	0	0	1.30	1.30
Perfume	0	0	0.30	0.30
Caffeine	0	1	0	1
L-Tartatic Acid	0	3	0	3
Water and minors	100%	To 100%	To 100%	To 100%

### Experimental Methodology

- 5 Set of swatches of hair were made from naturally curly hair. The initial length of all the swatches were measured before the treatment by taking a photograph and using a ruler ( $L_0$ ). The swatches were cleaned using a base shampoo. The treatment protocol was as follows. All swatches were treated
- 10 twice with 9%w/w of a shampoo by massaging the shampoo into the hair for 30 seconds and then rinsing for 30 seconds. Thereafter, 18%w/w of a conditioner was applied by massaging it to the hair for 60 seconds and then rinsing it for 60 seconds. Thereafter, the switches were treated with

- 22 -

Examples 1 and A by soaking the switch in these Examples for 15 minutes, shaking off excess water and finally combing it before leaving it to dry at 20°C, 50RH for 3hours. At this stage the length of the swatches were measured ( $L_1$ ).

5 Furthermore, a final length of the swatches ( $L_1$ ) were measured after exposure to 30°C, 80RH for 3hours.

For Examples 2 and B the switches were treated with 9%w/w of these products by massaging them into the hair switches,  
10 combing these switches straight and leaving them to dry. All swatches after treatment were dried under controlled environment of 20°C, 50RH for 3hours.

Once the swatches were dry their length was measured again,  
15 and the swatches were moved to a new environment of 30°C and 80RH for 3 hours. A third and final measurement of the length of the swatches was made. In case of treatment of swatches with Examples B and 2, the comparisons were made after 8 treatment cycles.

20

The following formula was used for converting the length measurements into % lengthening against control (Example A or Example B). The results are shown in the table below.

$$\% \text{Lengthening}_{20^\circ\text{C}, 50\text{RH}} = \left[ \left( \frac{L_{1i} - L_{0i}}{L_{1i}} \right) - \left( \frac{L_{1j} - L_{0j}}{L_{1j}} \right) \right] * 100$$

25 where, i stands for Examples according to the invention (1 and 2) and j stands for the comparative Examples (A and B), respectively.

- 23 -

Formulation	% Lengthening after drying @20°C, 50RH	% Lengthening after exposure @30°C, 80RH
Example 1 vs Example A	13.86	9.67
Example 2 vs Example B	7.74	6.72

Examples C, D, E , F, 3 and 4

5

Solutions were formulated each containing 1% by weight of the examples. Hair curls were made up using perming rods and 30cm length hair. The curls were placed in the solution for 1 hour, rinsed thoroughly with distilled water and dried for 30 minutes. The hair was removed from the curling rod and the length of the curl measured. The hair was hung in high humidity environmental chamber (90%RH, 30°C) with fan agitation for 1 minute and measured again.

15



- 24 -

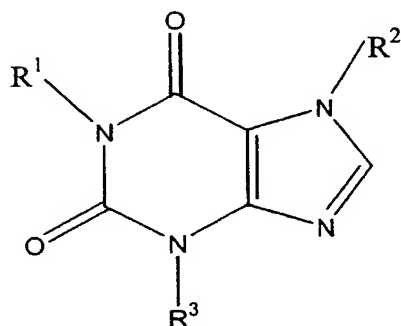
Experiment	Styling Compound	Weight Percent	Solvent	Comments	Curl Drop Out Value (% increase in length) Drop Out Value (% increase in length)
Negative Control	Water	100%	Water		64
Positive Control	Commercial Hairspray	N/A	N/A	At least 2 actuations of spray applied to each side of curl	45.4
Example C	Caffeine	1%	Water	/	48
Example D	Caffeine	5% (at 50°C)	Water	/	45.8
Example E	Citric Acid	1%	Water	/	49
Example F	Citric Acid	5%	Water	/	37.5
Example 3	Caffeine + Citric Acid	1% of each (at room temperature)	Water	/	35
Example 4	Caffeine + Citric Acid	5% of each (at 50°C)	Water	/	16.8

CLAIMS

1. A method of treating hair comprising the step of  
5 applying to the hair a leave on hair treatment  
composition comprising:

i) an  $\alpha$ -hydroxy acid, its salt or mixtures thereof; and  
ii) a xanthine, substituted xanthine or mixtures  
10 thereof.

2. A method according to claim 1 in which the xanthine  
substituted xanthine ii) of the hair treatment  
composition has the following formula:



in which  $R^1$ ,  $R^2$  and  $R^3$  are independently selected from H,  
substituted or unsubstituted  $C_1$ - $C_5$  alkyl groups,  
substituted or unsubstituted  $C_2$ - $C_5$  alkenyl groups, aryl  
20 groups, arylalkyl groups or mixtures thereof,

3. A method according to claim 2 in which  $R^1$ ,  $R^2$  and  $R^3$  of  
the xanthine/substituted xanthine ii) are independently  
selected from H,  $C_1$ - $C_5$  alkyl groups,  $C_2$ - $C_5$  alkenyl or  
25 mixtures thereof.

- 26 -

4. A method according to claim 3 in which  $R^1$ ,  $R^2$  and  $R^3$  of ii) are independently selected from H, methyl groups or mixtures thereof.

5

5. A method according to any preceding claim in which the xanthine derivative ii) is caffeine.

6. A method according to any preceding claim in which the  $\alpha$  -hydroxy acid and/or its salt i) is a citric acid and/or its salt.

10

15

7. A method according to any one of claims 1 to 5 in which the  $\alpha$  -hydroxy acid and/or its salt i) is a bis ( $\alpha$  -hydroxy acid) and/or its salt.

8. A method according to claim 7 in which the an  $\alpha$  -hydroxy acid i) is tartaric acid or its salt.

20

9. A method according to any preceding claim in which the an  $\alpha$  -hydroxy acid and/or its salt if optically active is in the L-form.

25

10. A method according to any preceding claim in which the total amount of acid/salt i) is from 0.1 to 20 wt% in the total formulation.

11. A method according to any preceding claim in which the total amount xanthine ii) is from 0.1 to 20 wt% in the total formulation.

30

- 27 -

12. A method according to any preceding claim in which the hair treatment composition further comprises a surfactant.
- 5 13. A hair treatment composition according to any preceding claim, in which the hair treatment composition further comprises a cationic, or silicone based conditioning agent.
- 10 14. A method according to any preceding claim in which the hair treatment composition further comprises a styling agent.
- 15 15. A method according to any preceding claim in which the hair treatment composition comprises an aqueous base.
16. Use of a composition as described in any preceding claim for styling the hair.
- 20 17. Use of i) an  $\alpha$ -hydroxy acid, its salts or mixture therefor; and ii) a xanthine, substituted xanthine or mixtures thereof for lengthening hair and or decreasing the volume of hair.
- 25 18. Use of a i) an  $\alpha$ -hydroxy acid its salts or mixtures thereof; and ii) a xanthine, substituted xanthine or mixtures thereof for increasing the high humidity style retention of hair.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/06648

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 A61K7/06 A61K7/09

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data, BIOSIS, EMBASE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 325 969 A (WOLFF CHEM PHARM GMBH) 2 August 1989 (1989-08-02) page 4, line 11 - line 20 page 4, line 55 - line 57 page 5, line 9 - line 11; claims ---	1-5, 10, 11, 15
X	FR 2 751 541 A (FABRE PIERRE DERMO COSMETIQUE) 30 January 1998 (1998-01-30) claims; example 4 ---	1-6, 11, 12, 15
A	EP 0 728 472 A (UNILEVER PLC ; UNILEVER NV (NL)) 28 August 1996 (1996-08-28) page 3, line 15 - line 22 page 3, line 40 - line 57 page 4, line 12 - page 5, line 12; examples --- -/--	1-11, 15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

6 October 2003

Date of mailing of the international search report

16/10/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Donovan-Beermann, T

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 03/06648

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US H1480 H (LUO XIAOCHUN) 5 September 1995 (1995-09-05) page - ---	1
A	WO 96 10387 A (GALLEY EDWARD ;BOOTS CO PLC (GB); BARTON STEPHEN PETER (GB)) 11 April 1996 (1996-04-11) the whole document ---	1
A	GB 2 321 595 A (KAO CORP) 5 August 1998 (1998-08-05) the whole document -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/06648

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0325969	A	02-08-1989	DE 3801034 A1 AT 88084 T DE 58904029 D1 DK 16389 A EP 0325969 A1 NO 890188 A , B, PT 89463 A , B	27-07-1989 15-04-1993 19-05-1993 16-07-1989 02-08-1989 17-07-1989 08-02-1990
FR 2751541	A	30-01-1998	FR 2751541 A1	30-01-1998
EP 0728472	A	28-08-1996	US 5523090 A CA 2168535 A1 EP 0728472 A2 JP 8253405 A ZA 9600740 A	04-06-1996 25-08-1996 28-08-1996 01-10-1996 31-07-1997
US H1480	H	05-09-1995	NONE	
WO 9610387	A	11-04-1996	AU 3744195 A WO 9610387 A2	26-04-1996 11-04-1996
GB 2321595	A	05-08-1998	DE 19533211 A1 CN 1199332 A WO 9709029 A1 JP 9110650 A TW 427910 B	08-02-1996 18-11-1998 13-03-1997 28-04-1997 01-04-2001

**THIS PAGE BLANK (USPTO)**



CORRECTED VERSION

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
15 January 2004 (15.01.2004)

PCT

(10) International Publication Number  
**WO 2004/004672 A1**

(51) International Patent Classification<sup>7</sup>: **A61K 7/06, 7/09**

Sheila, Anne [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).

(21) International Application Number:  
PCT/EP2003/006648

(74) Agent: TANSLEY, Sally; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).

(22) International Filing Date: 25 June 2003 (25.06.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
02254722.8 5 July 2002 (05.07.2002) EP

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(71) Applicant (*for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NI, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only*): **UNILEVER N.V.** [NL/NL]; Unilever N.V., Weena 455, NL-3013 AL Rotterdam (NL).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only*): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London, Greater London EC4 4BQ (GB).

Published:  
— with international search report

(71) Applicant (*for IN only*): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

(48) Date of publication of this corrected version:  
25 March 2004

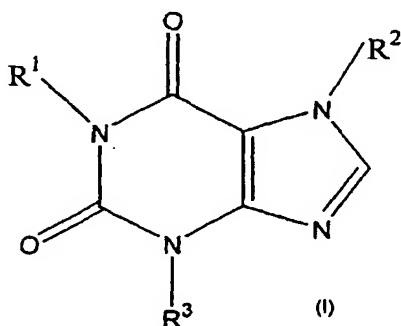
(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **KHOSHDEL, Ezat** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **WARD,**

(15) Information about Correction:  
see PCT Gazette No. 13/2004 of 25 March 2004, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HAIR TREATMENT COMPOSITIONS CONTAINING XANTHINE AND ALPHA HYDROXY ACID



(57) Abstract: The invention provides a hair treatment composition such as a shampoo or conditioner suitable for topical application to style hair and in particular to lengthening the hair. The composition comprises an  $\alpha$ -hydroxy acid and/or its salt and a xanthine preferably having the following formula.

**THIS PAGE BLANK (USPTO)**

**ORIGINAL  
NO MARGINALIA**